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(54) Name of the invention:

Manufacturing Method for Crystallized Glass

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Description of the invention

1. **Name of the invention**

Crystallized Glass Manufacturing Method

2. **Scope of the Claims**

(1) Crystallized glass manufacturing method where a glass material is obtained as a crystallized glass component, formed as, by weight %, SiO2: 5 ~ 50 %, Al2O3: 5 ~ 70 %, Y2O3: 10 ~ 70 % are contained as the main components, and among the MgO, TiO2, ZrO2, La2O3 etc., additive agents, at least one type or more is contained as a seed forming agent, is melted and slowly cooled, or as the molten solution is rapidly cooled; and this glass material is then subjected to a thermal treatment at a temperature in the range of 900 ~ 1250oC for a period that is within 100 hours, and by that micro-crystals are separated.

(2) Crystallized glass manufacturing method where in order to mix homogeneously the powder material with the composition according to the above Claim paragraph (1), relative to 100 weight parts of the raw material component fine powder material with an average particle diameter in the range of 0.1 ~ 300 microns, as a solvent media, water or organic solvent is added in an amount that is in the range of 20 ~ 150 weight parts, and in order to homogeneously disperse the powder, water soluble acrylic resin, polyethylene glycol, polyethylene amine, anionic type polymer etc., organic material component is added in an amount in the range of 0.1 ~ 10 weight parts, and the mixed ceramics powder is homogeneously mixed and dispersed, and after that the solvent agent is evaporated and a homogeneously mixed powder is obtained, and this is heated to a temperature in the range of 300 ~ 700oC, and the resin is eliminated, and after that it is melted at a high temperature and it is slowly cooled or the molten solution is rapidly cooled, and the obtained by that glass material is then subjected to a thermal treatment at a temperature in the range of 900 ~ 1250oC for a period that is within100 hours, and by that micro-crystals are separated.

3. Detailed Description of the Invention

[Technological Field of Application]

The present invention is an invention about the manufacturing method for the production of crystallized glass with high hardness and with excellent heat resistance and corrosion resistance properties. And especially, the present invention is an invention about the manufacturing method for the production of the same glass that can be effectively and appropriately used in the manufacturing of heat resistant, wear resistant ceramics dials or ceramics substrate plates, containers, etc.

[Previous Technology]

The manufacturing method for the production of the glass according to the previous technology is simple, however, there has been the drawback that at high temperatures of several hundreds of degrees Celsius and above, it undergoes softening, etc. Among these materials, the glass materials containing SiO2, Al2O3, Y2O3 as their main components have a melting point of approximately 1350oC and higher, and they can be used as a glass material up to relatively high temperatures, however, even in the case of these materials, there has been the drawback that at temperatures of 900oC and above, there is softening. On the other hand, alumina, etc., sintered materials then can be used at high temperatures, however, it is necessary that they be sintered at high temperatures of 1700oC, and there is the drawback that the cost becomes high.

[Problem Points Solved by the Present Invention]

The present invention has taken into consideration the above described technology references, and it is an invention that is suggesting a method for the preparation of crystallized ceramics material, where in order to decrease the effect of the softening of the glass at high temperature, fine crystals of alumina, garnet etc., are separated in large amounts, and through that the heat resistance properties obtained are high and this material can be used even at relatively high temperatures of several hundred degrees C; and also, where the raw material powder is finely pulverized and it is homogeneously mixed in advance and by that the time period of the homogenization heat treatment of the molten solution at a high temperature is made shorter, and as the high temperature technological process is made shorter compared to the glass manufacturing method according to the previous technology, a method for obtaining crystallized ceramics material with homogeneously dispersed fine crystals, is suggested. Also, in order to separate a large amount of fine crystals, usually, it is necessary to generate a large number of crystal seeds (nuclei), and because of that through the addition of additive agents that are materials, which easily become crystalline nuclei for crystalline growth, it is an invention that suggests a method for the promoting of the glass crystallization.

Because of that, the present invention is an invention that produces ceramics with different types of compositions, and that first practically investigates the composition

range of the region where the necessary for the generation of crystallized glass, unknown up to now, high temperature solid phase and a liquid phase co-exist, and then it is an invention that clarifies the conditions for the crystallization of the glass phase.

[Measures in Order to Solve the Problems]

The present invention is a crystallized glass manufacturing method where a glass material is obtained as a crystallized glass component, formed as, by weight %, SiO2: 5 ~ 50 %, Al2O3: 5 ~ 70 %, Y2O3: 10 ~ 70 % are contained as the main components, and among the MgO, TiO2, ZrO2, La2O3 etc., additive agents, at least one type or more is contained as a seed forming agent, is melted and slowly cooled, or as the molten solution is rapidly cooled; and this glass material is then subjected to a thermal treatment at a temperature in the range of 900 ~ 1250oC for a period that is within100 hours, and by that micro-crystals are separated. And also, the present invention is a crystallized glass manufacturing method where in order to mix homogeneously the powder material with the composition according to the above Claim paragraph (1), relative to 100 weight parts of the raw material component fine powder material with an average particle diameter in the range of 0.1 ~ 300 microns, as a solvent media, water or organic solvent is added in an amount that is in the range of 20 ~ 150 weight parts, and in order to homogeneously disperse the powder, water soluble acrylic resin, polyethylene glycol, polyethylene amine, anionic type polymer etc., organic material component is added in an amount in the range of 0.1 ~ 10 weight parts, and the mixed ceramics powder is homogeneously mixed and dispersed, and after that the solvent agent is evaporated and a homogeneously mixed powder is obtained, and this is heated to a temperature in the range of 300 ~ 700oC, and the resin is eliminated, and after that it is melted at a high temperature and it is slowly cooled or the molten solution is rapidly cooled, and the obtained by that glass material is then subjected to a thermal treatment at a temperature in the range of 900 ~ 1250oC for a period that is within 100 hours, and by that micro-crystals are separated.

[Effect]

Regarding the glasses that have Al2O3, Y2O3, SiO2 as their main components, and that do not contain Na, K, etc., alkali metals, compared to the usual alkali glass materials, they have the characteristics where it is said that both the softening point temperature and the melting point temperature, are high, however, in order to improve the heat resistant properties and the hardness, etc., properties, it is necessary that a large amount of high hardness alumina Al2O3 or garnet Al5Y3O12, etc., be separated. Because of that, through the optimization of the composition range of the main components, the added amount of the seeding agents, the method for the mixing of the fine raw material powder material, it has been possible to achieve the desired goals. Here below, an explanation regarding these effects will be provided.

(1) As main components, as weight %, SiO2: 5 ~ 50 %, Al2O3: 5 ~ 70 %, YeO3: 10 ~ 70 %, are contained. In the case of the compositions outside of these ranges, there is no formation of glass, or because the amount of the generated liquid phase that is in a co-existence state with the high temperature solid solution is extremely

small, there is only a generation of sintered material, and because of that there is the drawback that even if it is heated at a high temperature of up to 1700oC no experimental material is obtained. Moreover, even within this compositional range, in order to separate a large amount of alumina or garnet etc., crystals, especially, it is necessary to select the concentration of the SiO2 to be within the range of 5 ~ 30 %.

(2) As the seeding agents, at least one type or more of MgO, TiO2, ZrO2, La2O3, etc., oxide materials is added in an amount in the range of 0.1 ~ 30 %. In the case when the added amount is less than 0.1 %, there is no crystallization promoting effect at all, and also, in the case when the amount added exceeds 30 %, the problems appears that also because of the crystallization promoting effect, the melting point also becomes low, and that is why these options are not preferred. Also, because of the fact that with the increase of the number of types of the additive agents, the glass melting point is decreased, it is preferred that if possible the number of types of the seeding agents, be kept at one. Moreover, the fact that the effect of the seeding agent is due to the strong trend that the additive agent is dissolved in the glass and a multi-element type solid solution is formed, and through a crystallization thermal treatment, the glass is microscopically phase separated and by that the separation of Al2O3, or Al5Y3O12 etc., crystals, is promoted, will be confirmed by the described her below practical implementation examples.

(3) The crystallization thermal treatment is conducted as the material is heated at a temperature that is in the range of 900 ~ 1250oC, and this is maintained for a period that is within100 hours. In the case when there is no addition of a seeding agent, the crystallization occurs at a temperature approximately in the range of 1000 ~ 1270oC, however, if a seeding agent is added, the crystallization can be conducted at a lower temperature. Also, it is a good option if the duration of the thermal treatment is within 100 hours. The reason for that is that by only heating at this temperature, the crystallization proceeds partially, and also, that by a thermal treatment with a duration within 100 hours, the crystallization is completed, and even if it is heat treated beyond that, the degree of crystallization is not increased. Moreover, in order to promote the crystallization, the method where the glass is again heated at high temperature, and besides that method, whereby the heated and melted at a high temperature molten solution in an electric kiln is slowly cooled at a rate of 20oC/min, or less, lead to the same results.

(4) The technological process used in order to homogeneously mix the fine raw material powder, has the described below results. The particle diameter of the raw material powder is made to be within the range of 0.1 ~ 300 microns. In the case of particles that are smaller than that, the cost of the fine and ultra-fine particles is high, and also, in the case of large particles with a diameter larger than that, longer time is required for melting in order to achieve homogeneous material during the melting of the glass, and because of that such size are not appropriate.

Preferably, powders with submicron particle diameter are used, and by that, it is possible to shorten the melting time during the manufacturing process. Relative to 100 weight parts of the raw material powder, solvent agent is added in an amount in the range of 20 ~ 150 weight parts, and an organic material is added in an amount in the range of 0.1 ~ 10 weight parts. In the case when the amount of the solvent agent is less than 20, the flow properties of the mixed material are not good, and also, even when solvent amount in excess of 150 is added, the mixed material is already in a suspension state and then the further addition of a solvent medium is not necessary. Regarding the organic material, any material is a good option as long as it has a dispersing effect relative to the powder materials used as the main components, and regarding the added amount, if it is less than 0.1, the effect is small, and also, if it is more than 10, the time for the removal of the resin becomes long, and there is the problem that it is said that the amount added is higher than the required amount. It is preferred that the technological process of the mixing of the raw material powder is done according to the described here below.

(5) If the obtained, organic material component containing mixed powder material is heated in the atmosphere or under reduced pressure, at a temperature in the range of 300 ~ 700oC, the organic material component is destructed and transformed into a gas phase and because of that the resin is removed, or regarding this process, it is also a good option if the powder material is heated inside an electric kiln, and the removal of the organic material is made to be one part of the melting technological process, and thus it is not necessary to define a specific resin removal technological process. Also, regarding the heating and melting conditions for the powder material, for example, it is a good option if it is heated at a temperature that is in the range of 1300 ~ 1500oC, for a period in the range of 0.1 ~ 5 hours, in an alumina kiln container. In order to generate glass material, it is necessary that a liquid phase is present at a high temperature, and because of that regarding the heating temperature, there are no specific limitations required as long as it is said to be a temperature where a molten solution is present. Moreover, in the case when the used solvent medium is water, as an organic material component, it is a good option to use water soluble acrylic resin, anionic type polymer, etc., and if the solvent medium is an organic solvent medium, it is possible to use soluble in the solvent medium polyethylene imine, etc., polymer material or a surface active agent. Moreover, from a cost point of view, the method where water is used for the dispersing process is preferred because of its low cost.

[Practical Examples]

As one practical implementation example of the present invention, an example regarding a manufactured crystallized glass example is explained here below.

A mixed powder material where relative to 100 weight parts of raw material powder with a composition defined as it is shown according to Table 1, and with a submicron particle

diameter, 50 weight parts of water, and 2 weight parts of anionic type polymer, are added, and this is mixed in a container for 20 hours, and a powder material where as the solvent 100 weight parts of ethanol are added, and 2 weight parts of polyethylene amine (this is amine, and above it was imine, could also be a typo – Translator's note) are added, and mixed for 20 hours, and powder materials were produced.

These powder materials were heated at a temperature of 500oC and at a vacuum of 0.1 Torr for a period of 1 hour, and after that, through the observed results from the variation of the diffraction intensity of the powder material measured by X-ray diffraction method, it was confirmed that the powder material was homogeneously mixed.

This mixed powder materials were placed inside alumina kiln containers, an as a temperature of 1500oC was maintained, they were heated for a period of 1 hour, and after that they were rapidly cooled, and the obtained glass materials were heat treated at a temperature of 1100oC for a period of 2 hours, and the crystallized glass materials shown according to Table 2, were obtained.

Moreover, as another practical implementation example, the Experimental material 4 was heated at a temperature of 1500oC for 1 hour and melted, and after that it was slowly cooled at a rate of 10oC/min, and by that it was possible to obtain the same white color crystallized glass material.

As it is shown according to Table 2, it was observed that in the case when a seeding agent was added, the crystallization initiation temperature of the glass phase that was obtained through the rapid cooling of the solid solution co-existence state (Experimental materials 4, 5 and 6) became lower compared to the experimental materials where there was no addition of seeding agents (8), and because of that, it was understood that MgO, TiO2, ZrO2, etc., oxide materials are effective in promoting the crystallization. Moreover, according to the method used in the previous technology, in the case when glass has been synthesized from powder material with a particle diameter of 100 microns, in order to produce homogeneous glass material, it has been necessary to maintain the material for a long time at the molten state, however, if the submicron level fine powder material is pre-dispersed in advance, even if it is heated at a temperature of 1500oC for a period of only 0.1 hours, a sufficiently homogeneous glass is obtained, and it was understood that the results of the present invention have a large effect on the used fine raw material powders. The glass transition point temperature of the obtained glass is approximately 900oC, however, through the separation of a large amount of crystals it is possible to increase the crystallization temperature to approximately 1000oC, and it is understood that a simple method is discovered whereby through only a simple heating in an electric kiln, high thermal resistance, and high hardness ceramics materials are obtained. Moreover, there is an amount of SiO2 inside the glass, however, it was understood that by making the amount of the SiO2 in the range of 30 ~ 50 %, crystalline SiO2 is separated inside the glass, and on the top of that, it is connected to the vitrification region. Also, in the case of glasses with different types of compositions, it was judged that in order to have a separation of fine crystals of high hardness Al2O3 or Al5Y3O12, the concentration of the SiO2 must be at or below 30 %.

Table 1

Composition of the Raw Material Powder and Powder Preparation Conditions

(The concentration is in weight %, the compounded amounts are shown as values relative to 100 weight parts of the ceramics powder material.)

Experimental Material Number	SiO2 Conc.	Al2O3 Conc.	Y2O3 Conc.	Seeding Agent Conc.	Solvent Compounded Amount	Organic Material Compounded Amount
1	24	42	29	ZrO2:5	Water:50	Anion type polymer:2
2	19	47	29	"	"	"
3	"	"	"	"	Ethanol:100	Polyethylene amine:2
4	19	29	47	ZrO2:5	Water:50	Anion type polymer:2
5	"	"	"	MgO:5	"	"
6	"	"	"	TiO2:5	"	"
7	19	24	53	ZrO2:4	"	"
8	20	30	50	Not added	"	"

Table 2

Conditions of the Preparation of the Crystallized Glass and Properties

(The melting conditions are 1 hour at 1500oC)

Experimental Material Number	Crystallization Heat Treatment	Separated Main Crystals	Crystallization Initiation temperature (oC)	Vickers Hardness (Gpa)
1	1100oC, 2 hr	A, M	950	8.3
3	"	A, G	1000	8.5
4	"	G, YS	960	8.5
5	"	"	940	8
6	"	"	950	8.3
7	"	YS, G	950	10
8	"	G, YS	1010	7.5

(Results From the Invention)

By using fine powder material as the raw material and by adding a seeding agent, it is possible to manufacture a high thermal resistance and high hardness crystallized glass material, and it has high merits from the point of view of the technological sphere of wear resistant parts that can be used at high temperatures, etc. Within the present invention, especially, due to the crystallized glass manufacturing utilizing the homogeneous dispersing of the fine powder material in advance, there is also the result that glass melting technological process becomes simple etc., and that leads to a decrease of the manufacturing costs, and then, in the case of this crystallized glass material, there is no alkali, and compared to the usual alkali glass, it is chemically stable, and the durability properties relative to corrosive ambient environments, are also increased.

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⑤発明の名称　結晶化ガラスの製造方法

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明　細　書

1. 発明の名称

結晶化ガラスの製造方法

2. 特許請求の範囲

(1) 重量%で、SiO_2：5～50%、Al_2O_3：5～70%、Y_2O_3：10～70%を主成分として含有し、MgO，TiO_2，ZrO_2，La_2O_3等の添加剤のうち1種以上を0.1～30%核形成剤として含有する結晶化ガラス成分を溶融して、徐冷するか、または溶融した溶液を急冷して得られたガラスを900～1250℃の温度で100時間以内の熱処理により微結晶を析出させることを特徴とする結晶化ガラスの製造方法。

(2) 請求項(1)の組成の粉末を均一に前もって混合するため、平均粒径0.1～300μmの原料成分微粉末100重量部に、溶媒として水または有機溶媒を20～150重量部、粉末を均一に分散させるため水溶性アクリル樹脂、ポリエチレングリコール、ポリエチレンアミン、アニオン系高分子等の有機質成分を0.1～10重量部加え、混合してセラミックス粉末を均一に混合して分散させた後、溶媒を蒸発させた均質に混合された粉末を得、これを300～700℃の温度に加熱して脱脂した後、高温で溶融して徐冷するか、または溶融した溶液を急冷して得られたガラスを900～1250℃の温度で100時間以内の熱処理により微結晶を析出させることを特徴とする結晶化ガラスの製造方法。

3. 発明の詳細な説明

〔産業上の利用分野〕

本発明は高硬度で耐熱性、耐食性に優れた結晶化ガラスの製造方法に関し、特に耐熱性で耐摩耗性のセラミックスタイルやセラミックス基板、容器等の製造に有利に適用が可能である同ガラスの製造方法に関する。

〔従来の技術〕

従来ガラスは製造法が簡単であるが、数百℃以上の高温では軟化する等の欠点があった。そ

の中でSiO_2, Al_2O_3, Y_2O_3を主成分とするガラスは融点も約1350℃以上でガラスとしては比較的高温まで使用できるが、それでも900℃以上では軟化する欠点があった。一方、アルミナ等の焼結体はさらに高温まで使用できるが、1700℃程度の高温で焼結しなければならず、価格が高くなるという欠点があった。

〔発明が解決しようとする問題点〕

本発明は上記技術水準に鑑み、高温でのガラスの軟化の影響を少なくするため、アルミナ、ガーネット等の微結晶を大量に析出させることにより、耐熱性を高め数百℃の比較的高温でも使用できるようにすること、また原料粉末を微粉末にしこれを均一に前もって混合しておくことにより、高温の融液での均一化熱処理時間を短くして従来のガラス製造法よりも高温での工程を短縮しながら、均質で微細な結晶を分散させた結晶化セラミックスを得る方法を提供しようとするものである。また、微細な結晶を多く析出させるためには一般的には結晶核を数多く発生させる必要があり、このため結晶成長の結晶核となりやすい物質を添加剤として加えることにより、ガラスの結晶化を促進しうる方法を提供しようとするものである。

このため、本発明は種々の組成のセラミックスを作製し、結晶化ガラスを生成させるために必要な今まで未知であった高温での固相と液相との共存領域の組成幅をまず実験的に究明し、つづいてガラス相を結晶化させる条件を明らかにしたものである。

〔問題点を解決するための手段〕

本発明は重量%でSiO_2：5～50%、Al_2O_3：5～70%、Y_2O_3：10～70%を主成分として含有し、MgO, TiO_2, ZrO_2等の添加剤のうち1種以上を0.1～30%核形成剤として含有する結晶化ガラス成分を溶融して、徐冷するか、または溶融した溶液を急冷して得られたガラスを900～1250℃の温度で100時間以内の熱処理により微結晶を析出させ結晶化ガラスを作製する方法である。また、本発明は上記組成の粉末を均一に前もって混合するため、平均粒径0.1～300μmの原料成分微粉末100重量部に、溶媒として水またはアルコール、ベンゼン、キシレン等の有機溶媒を20～150重量部、粉末を均一に分散させるため水溶性アクリル樹脂、ポリエチレングリコール、ポリエチレンアミン、アニオン系高分子等の有機質成分を0.1～10重量部加え、混合してセラミックス粉末を均一に混合して分散させた後、溶媒を蒸発させた均質に混合された粉末を得、これを300～700℃の温度に加熱して脱脂した後、高温で溶融して徐冷するか、または溶融して溶液を急冷して得られたガラスを900～1250℃の温度で100時間以内の熱処理により微結晶を析出する結晶化ガラスの製造方法である。

〔作用〕

Al_2O_3, Y_2O_3, SiO_2を主成分とするガラスでNa, K等のアルカリ金属を含有しないガラスは、通常のアルカリガラスと比較し、軟化温度や融点も高いという特徴をもつが、耐熱性や硬度等の特性を改善するためには、硬度の高いアルミナAl_2O_3やガーネット$Al_5Y_3O_{12}$等の結晶を多量に析出させる必要がある。このため主成分の組成範囲、核形成剤の添加量、原料微粉末の混合方法を最適化させることにより所期の目的を達成できた。以下にその作用について説明する。

(1) 主成分として重量%でSiO_2：5～50%、Al_2O_3：5～70%、Y_2O_3：10～70%を含有する。これ以外の組成ではガラスが生成しないか、又は高温の固液共存状態で液相の生成量が非常に少なく焼結体しか生成しないため、1700℃前後の高温にまで加熱しなければ試料が得られない欠点を有する。なおこの組成範囲の中でも、アルミナやガーネット等の結晶を多く析出させるためには、特にSiO_2濃度は5～30%に選ぶことが必要である。

(2) 核形成剤としてMgO, TiO_2, ZrO_2, La_2O_3等の酸化物を1種以上0.1～30%添加する。

添加量として0.1%以下では結晶化促進効果があまりなく、また30%以上多量に加えた場合は、結晶促進効果よりも融点が低くなる方が問題となるので好ましくない。また添加剤の種類を多く加えるとそれだけガラスの融点が低くなるので、核形成剤の種類はできれば1種が好ましい。なお核形成剤の効果としては、添加剤がガラス中に溶けて多元系の固溶体を生成し、結晶化熱処理によりガラスが微視的に分相をおこす傾向を強めることにより、Al_2O_3 や$Al_5Y_3O_{12}$等の結晶の析出を促進させるという作用として働くことが後述の実施例にて確認された。

(3) 結晶化熱処理は900～1250℃に加熱し、100時間以内保持する。核形成剤を添加しない場合、結晶化は1000～1270℃くらいの温度で起こるが、核形成剤を添加すればさらに低温側で結晶化が可能である。また熱処理時間は100時間以内でよい。これはその温度に加熱するだけでも結晶化は部分的に進み、また100時間以内の熱処理時間で結晶化は完了するので、これ以上熱処理しても結晶化度は増えない。なお結晶化を進めるためには、ガラスを再び高温へ加熱する方法以外に、高温に加熱溶融した融液を電気炉中で冷却速度20℃/min以下のゆっくりした速度で徐冷しても同様の効果が得られる。

(4) 原料微粉末を均一に混合するための工程は以下のような効果を有している。原料粉末の粒径は0.1～300μmとする。これより微細な超微粒子はコスト高であり、またこれより大きい粗粒はガラス溶融時に均質にするため長時間の溶融を要するので不適当である。好ましくは粒径サブミクロン程度の粉末を用いることにより、製造上の溶融時間を短縮することができる。原料粉末100重量部に溶媒20～150重量部、有機質0.1～10重量部を加える。溶媒量が20以下では混合物の流動性がよくなく、また150以上加えても混合物はけん濁液のままであり、それ以上溶媒をさらに追加する必要はない。有機質は粉体を主として分散させる効果をもてばよいので、添加量としては0.1以下では効果が少なく、また10以上では脱脂時間が長くなり、必要量以上に加えているという問題点がある。原料粉体の混合工程は以上のようにするのが好ましい。

(5) 得られた有機質成分を含む粉末混合物を大気中又は減圧下で300～700℃に加熱すれば、有機質成分は分解し気化するので脱脂されるが、この工程は粉末を電気炉で加熱し、溶融する工程の一部としてもよく、特に脱脂工程を設定する必要はない。また粉末を加熱し、溶融する条件は例えば1300～1500℃の温度に0.1～5時間アルミナるつぼ中で加熱すればよい。ガラスを生成させるためには高温で液相が現われることが必要であり、このため加熱温度としては融液が現われる温度ということで特に限定する必要はない。なお用いた溶媒が水の場合、有機質成分としては水溶性アクリル樹脂、アニオン系高分子等がよく、溶媒が有機溶媒であれば溶媒にとけるポリエチレンイミン等の高分子や界面活性剤が使用できる。なおコスト的には水に分散させる方がより安価である。

〔実施例〕

本発明の一実施例として作製した結晶化ガラスの例を以下に説明する。

表1に示したように所定の組成の粒径サブミクロンの原料粉末100重量部に、水50重量部、アニオン系高分子2重量部を加え、容器中で20時間混合した粉末と、溶媒としてエタノール100重量部、ポリエチレンアミン2重量部を加え、20時間混合した粉末を作製した。

これら粉末は0.1Torrの真空度で500℃で1時間加熱保持したのち、X線回折により粉末の回折強度のばらつきを調べた結果、粉末はいずれも均一に混合されているのが確認された。この混合粉末をアルミナるつぼに入れ、1500℃で1時間加熱保持した後急冷し、得られたガラ

スを、１１００℃で２時間熱処理して表２に示すような結晶化ガラスを得た。

なお、別の実施例として試料４を１５００℃で１時間加熱溶融した後、１０℃／min の速度で徐冷することにより白色の結晶化ガラスを同様に得ることができた。

表２に示すように、核形成剤を添加した場合、固液共存状態が急冷されて得られたガラス相の結晶化開始温度（試料４，５，６）は無添加の試料（８）と比較して、低くなっているのが見られたので、MgO，TiO₂，ZrO₂ 等の酸化物は結晶化促進に有効であることがわかった。なお従来法により粒径１００μm 程度の粉末からガラスを合成する場合、均一なガラスを作成するためには溶融状態で長時間保持する必要があったが、サブミクロン程度の微粉末を均一に前もって分散させておけば、１５００℃で0.1時間程度加熱するだけでも十分に均質なガラスが得られ、原料微粉末を使用した本発明の効果が大きいことがわかった。得られたガラスのガラス転移温度は約９００℃であるが、結晶を多量に析出させることにより結晶化温度は約１０００℃にまで高くすることができ、耐熱性で硬度の高いセラミックスを電気炉で単に加熱するだけの簡単な手法で得られることがわかった。なおガラス中の SiO_2 量であるが、SiO_2 量が３０～５０％ではガラス中に結晶質 SiO_2 が析出し、それ以上ではガラス化領域からずれてくることがわかった。また種々の組成のガラスを、結晶化させた場合、硬度の高い Al_2O_3 や $Al_5Y_3O_{12}$ の微結晶を析出させるためには、SiO_2 濃度は３０％以下にする必要があることが判明した。

表　1

原料粉末の組成と粉末調整条件

（濃度は重量％、配合量はセラミックス粉末１００重量部に対する値を示す。）

試料番号	SiO_2濃度	Al_2O_3濃度	Y_2O_3濃度	核形成剤濃度	溶媒配合量	有機質配合量
1	24	42	29	ZrO_2 : 5	水 : 50	アニオン系高分子 : 2
2	19	47	29	〃	〃	〃
3	〃	〃	〃	〃	エタノール : 100	ポリエチレンイミン : 2
4	19	29	47	ZrO_2 : 5	水 : 50	アニオン系高分子 : 2
5	〃	〃	〃	MgO : 5	〃	〃
6	〃	〃	〃	TiO_2 : 5	〃	〃
7	19	24	53	ZrO_2 : 4	〃	〃
8	20	30	50	無添加	〃	〃

表　2

結晶化ガラスの作製条件と特性（溶融条件は1500℃ 1 hr）

（結晶名：A（Al_2O_3），G（Garnet），YS（$Y_2Si_2O_7$），M（Mullite））

試料番号	結晶化熱処理	析出した主な結晶	結晶化開始温度（℃）	ヴィッカース硬度（GPa）
1	1100℃、2hr	A，M	950	8.3
3	〃	A，G	1000	8.5
4	〃	G，YS	960	8.5
5	〃	〃	940	8
6	〃	〃	950	8.3
7	〃	YS，G	950	10
8	〃	G，YS	1010	7.5

〔発明の効果〕

原料として微粉末を用い核形成剤を添加することにより、耐熱性で高硬度の結晶化ガラスを製造することができ、高温で使用可能な耐摩耗部材等産業上の利用価値が高い。本発明の中で特に微粉末を前もって均一に分散させておくことにより結晶化ガラスを製造するための、ガラス溶融工程が簡単になるなど製造コスト低減への効果もあり、さらに本結晶化ガラスは無アルカリであり、通常のアルカリガラスと比較すると化学的に安定であり、腐食性雰囲気に対しても耐久性が改善されるので有用である。

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